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## A Search for Scintillation in Doped and Orthorhombic Lead Fluoride

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# **A Search for Scintillation in Doped and Orthorhombic Lead Fluoride**

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## **Abstract**

Samples of high-purity, orthorhombic  $\text{PbF}_2$  have been produced. A small amount of scintillation light was detected during gamma-ray excitation, but only at a level which is comparable to the Cherenkov light produced in cubic  $\text{PbF}_2$ . Samples of cubic and orthorhombic  $\text{PbF}_2$  with various dopants are also studied.

## 1 Introduction

$\text{PbF}_2$  has been investigated as a Cherenkov radiator for electromagnetic calorimetry for some time[1-3]. It has the advantages that it is dense ( $\rho = 7.77$ ), has a high average atomic number, is transparent into the near UV, and is relatively inexpensive. Though it excels as a Cherenkov radiator, it would be extremely useful for many applications if it could be made to scintillate with a reasonable light output and a short decay constant.

With the exception of the precipitated powder,  $\text{PbF}_2$  is normally found as a cubic crystal. At the Crystal 2000 International Conference on Heavy Scintillators for Scientific and Industrial Applications (Chamonix, France, September 22-26, 1992) there was a report on the observation of substantial scintillation from orthorhombic  $\text{PbF}_2$  [4]. By using a hot, mechanical press they were able to convert cubic  $\text{PbF}_2$  crystals from not more than 5% orthorhombic near the edge of the sample, to about 30% at the center. They claimed emissions from some regions of the material had scintillation yields of 20% of  $\text{NaI(Tl)}$ , implying a scintillation yield for pure orthorhombic  $\text{PbF}_2$  equivalent to that of  $\text{NaI(Tl)}$ . The emission spectrum extended from 350-550 nm, and decay times ranging from less than 15 ns to 30 ns, depending on the details of the material.

Scintillation from orthorhombic- $\text{PbF}_2$  powder had first been reported by Derenzo et al. [5], but with a much smaller intensity than claimed above. However, it was the recent results of Baliakin, et al. which led us to the investigation described below. Doped cubic and orthorhombic  $\text{PbF}_2$  are also studied

## 2 Doped cubic $\text{PbF}_2$

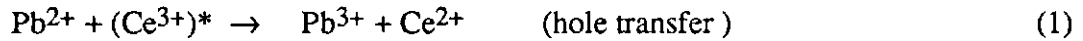
The  $\text{Pb}^{2+}$  ion belongs to the family of the  $6s_2$  ions, like  $\text{Tl}^+$  and  $\text{Bi}^{3+}$ . These ions are characterized by excitations from the  $^1S_0$  ground state to the  $^3P_1$ ,  $^3P_2$  and  $^1P_1$  excited states. The emission can be intense, particularly at low temperatures, but in general is very slow (in the msec range). This is because it originates from the  $^3P_0$  metastable state, through a transition which is strongly forbidden. On the other hand, if the energy gap between the  $^3P_0$  and the  $^3P_1$  level (the trap depth) is small compared to the thermal energy, when the temperature increases, the  $^3P_1$  state can also be populated. The relaxation to the ground state is then much faster because the transition is allowed by spin-orbit mixing of the  $^3P_1$  and  $^1P_1$  states. High temperature quenching, associated with a large Stokes shift, can further reduce the decay time, but also reduces the light yield.

In cubic  $\text{PbF}_2$  at liquid helium temperatures, an emission band at 303 nm can be excited in the region of intrinsic absorption of the lattice with a decay time of 214 ms. Two other bands at 285 nm and 525 nm are excited in the region of the absorption edge (230 nm to 260 nm) with decay times of 80 ms and 610 ms, respectively. The decay

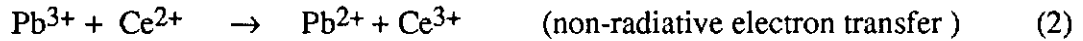
times of these three bands is rapidly decreasing above 20 K with a simultaneous decrease in intensity. No emission can be detected from cubic  $\text{PbF}_2$  at room temperature [6].

As the lattice parameter is relatively small (5.94 Å), the short Pb-Pb distances ( $\approx 4$  Å) give rise to a large wave function overlap, leading to energy migration through the lattice. This property can open the way to the trapping of the  $\text{Pb}^{2+}$  ion exciton on a well chosen luminescent impurity. We have therefore asked Optovac and the Shanghai Institute of Ceramics (S.I.C.) to introduce luminescent ions in the  $\text{PbF}_2$  lattice. The dopants studied, the band edge of the doped  $\text{PbF}_2$ , and the results of luminescence studies are given in Table I. The concentrations are 1% for all dopants where the concentration is not otherwise indicated. These concentrations are the concentration in the melt and may not be the concentration of the final product.

When excited in the region of excitation transitions of these ions, a slow luminescence signal could be seen in some cases, for ions with a small gap between the ground state and excited state ( $\approx 2$  eV). For higher transition energies to the excited state, like  $\text{Ce}^{3+}$  doping ( $\approx 4$  eV), no luminescence was detected. A mechanism of photoionization is probably responsible for the quenching of the Ce emission. This could be related to the rather small energy gap between the 6s and 6p orbitals of the  $\text{Pb}^{2+}$  ion (about 5 eV, compared to 4 eV for the  $4f \rightarrow 5d$  transition in  $\text{Ce}^{3+}$ ). The non-radiative process can be therefore described in the following way:



followed by:



For all the samples studied, no scintillation signal above the level of the Cherenkov emission could be detected when excited with different radioactive sources.

### 3 Orthorhombic $\text{PbF}_2$

$\text{PbF}_2$  is converted from the cubic to the orthorhombic phase under pressure, with the transition pressure being temperature dependent. Fig. 1 shows the transition temperature as a function of pressure for increasing and decreasing pressures at constant temperature, as well as for increasing temperature at constant pressure [7]. At 27 °C, the transition pressure is about 4 katm, while it is only about 1.4 katm at 175 °C.

Due to the fact that a hot, mechanical press was not available, an isostatic pressing technique was used, where the samples were put under pressure in a medium of either water or argon gas. For our first attempt, three samples of  $\text{PbF}_2$  were pressed by the

Department of Material Science and Engineering at Cornell University. These samples were placed in latex-rubber pouches and pressurized in water at room temperature to a pressure of about 7 kbar. Because of the reduction in volume when going from the cubic to orthorhombic phase ( $\approx 10\%$ ), the samples developed numerous micro cracks and had the appearance of polished white marble. This would certainly yield a very short attenuation length for any scintillation.

In order to obtain material with larger clear domains, a large piece of  $\text{PbF}_2$  was pressed by Industrial Materials Technology, Inc. (Andover, MA, U.S.A.). The sample was first heated to about  $540^\circ\text{C}$  at 34 atm of clean argon gas. The pressure was then increased to 2 kbar and maintained while the  $\text{PbF}_2$  was allowed to slowly cool. At  $100^\circ\text{C}$  the pressure was removed and the cooling allowed to continue. This allowed the sample to go through the cubic-to-orthorhombic transition at a high temperature while soft. The resulting material was an aggregate of clear domains with dimensions of 2-3 mm. X-ray diffraction studies performed on all of the samples of converted  $\text{PbF}_2$  showed them to be over 99% orthorhombic.

Fig. 2 show the luminescence spectra from three samples of  $\text{PbF}_2$  measured during  $^{60}\text{Co}$  irradiation at the Gamma Ray Irradiation Facility at Brookhaven National Laboratory. Curve A is the spectrum for a polished piece of cubic  $\text{PbF}_2$ . The spectrum is consistent with a Cherenkov spectrum with a cutoff at about 250 nm. Curve B is from one of the orthorhombic samples with micro cracks from the first conversion. No significant light output was seen, presumably due to the short attenuation length caused by the micro cracks. Curve C is the emission spectrum for the piece of orthorhombic material from the second pressing. The change in shape indicates that there may be a scintillation component in the spectrum, but with a very low intensity.

Since the light output observed from the orthorhombic samples during irradiation was extremely weak, it was difficult to distinguish between any scintillation activity and Cherenkov light. However, in such a case, it is often useful to try and determine if there are any other types of luminescent centers in the material by measuring thermoluminescence. Often, the same general recombination processes which produce thermoluminescence can also produce luminescence during irradiation. Fig. 3 shows the thermoluminescence spectra obtained for the same three samples of  $\text{PbF}_2$  samples studied in fig. 2. The measurements were made approximately 15 minutes after irradiation to  $2 \times 10^5$  rad with  $^{60}\text{Co}$  gamma rays. Generally, each peak and inflection point on the curves represent a separate thermally-activated process in the material, corresponding to the release of electrons or holes from a trap, and migration to a luminescent recombination center. The level of the thermoluminescence signal in the orthorhombic samples is considerably larger than in the cubic sample. This indicates a greater number

of recombination centers in the orthorhombic material, which are probably due to a much higher concentration of defects and/or other traps. Although the amount of thermoluminescence of the orthorhombic samples is higher than for the cubic sample, the levels are still smaller than what has been measured for a number of other materials.

Samples of  $\text{PbF}_2$  doped at levels in the range of 0.5-1% with Ce, Nd, Tb, Dy, Ho, Er, and Tm were also converted to the orthorhombic form. Although most of them fluoresced brightly under a UV lamp, no significant scintillation was detected from ionizing radiation. Only the Tb sample showed a series of weakly luminescent emission peaks, which were in rough agreement with those given in Table I.

#### **4 Conclusion**

An investigation of doped cubic  $\text{PbF}_2$  has proved unsuccessful in producing significant scintillation. Samples of  $\text{PbF}_2$ , which are in excess of 99% orthorhombic, have been produced by a hot, isostatic pressing technique. A small amount of luminescence was seen in the orthorhombic material, but its intensity is small compared to the Cherenkov light. Our results are more consistent with those of Derenzo et al. than with Baliakin et al. Initial attempts to see significant scintillation from rare-earth doped orthorhombic  $\text{PbF}_2$  have also been fruitless. Although the initial attempts to produce scintillation in pure orthorhombic  $\text{PbF}_2$  have not been encouraging, additional investigations with doped orthorhombic  $\text{PbF}_2$  may be worthwhile.

**Table I: Properties of doped, cubic PbF<sub>2</sub> crystals**

<b>Producer</b>	<b>Dopant**</b>	<b>Band-edge</b>	<b>Luminescence</b>
Optovac, Inc.	none	260 nm	no
Optovac, Inc.	Ba	330 nm	weak 358 nm
Optovac, Inc.	Tb	260 nm	slow 384, 414, 434, 487, 542 nm
Optovac, Inc.	Bi	260 nm	no
Optovac, Inc.	Co	350 nm	no
Optovac, Inc.	Ag	260 nm	no
Optovac, Inc.	Cu	305 nm	no
Optovac, Inc.	Cr	260 nm	no
Optovac, Inc.	Dy	260 nm	slow 448 nm, 512 nm,
Optovac, Inc.	Sm		slow 564, 594, 600 nm
Optovac, Inc.	Yb		weak 405 nm
Optovac, Inc.	Eu		slow 467, 510, 589, 619 nm
Optovac, Inc.	Nd 0.5%		no
Optovac, Inc.	Ho 0.5%		no
Optovac, Inc.	Er 0.5%		no
Optovac, Inc.	Tm 0.5%		no
S.I.C.	none	260 nm	no
S.I.C.	Ce 100 ppm	315 nm	no
S.I.C.	Ce	325 nm	no
S.I.C.	Ba 10% Ce 0.1%	325 nm	no
S.I.C.	Ba 20% Ce 0.1%	315 nm	no
S.I.C.	Ce	325 nm	no
S.I.C.	Ce	325 nm	no

\*\*All dopants without concentrations are 1%.

### Acknowledgments

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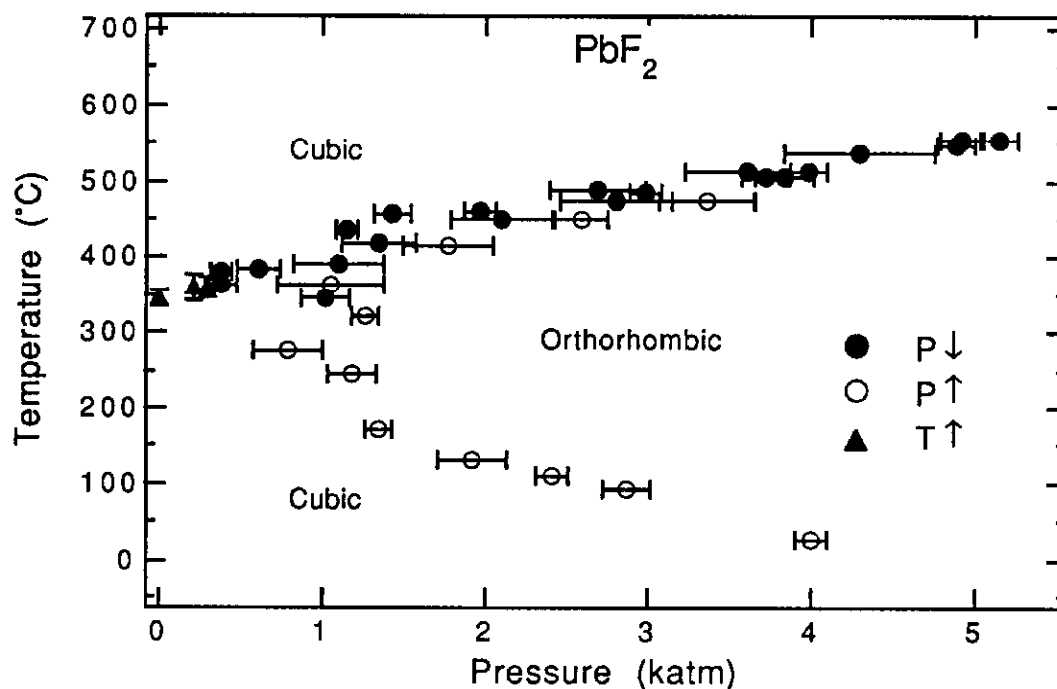


Figure 1 Transition temperature of  $\text{PbF}_2$  as a function of pressure for increasing and decreasing pressures at constant temperature, as well as for increasing temperature at constant pressure [7].

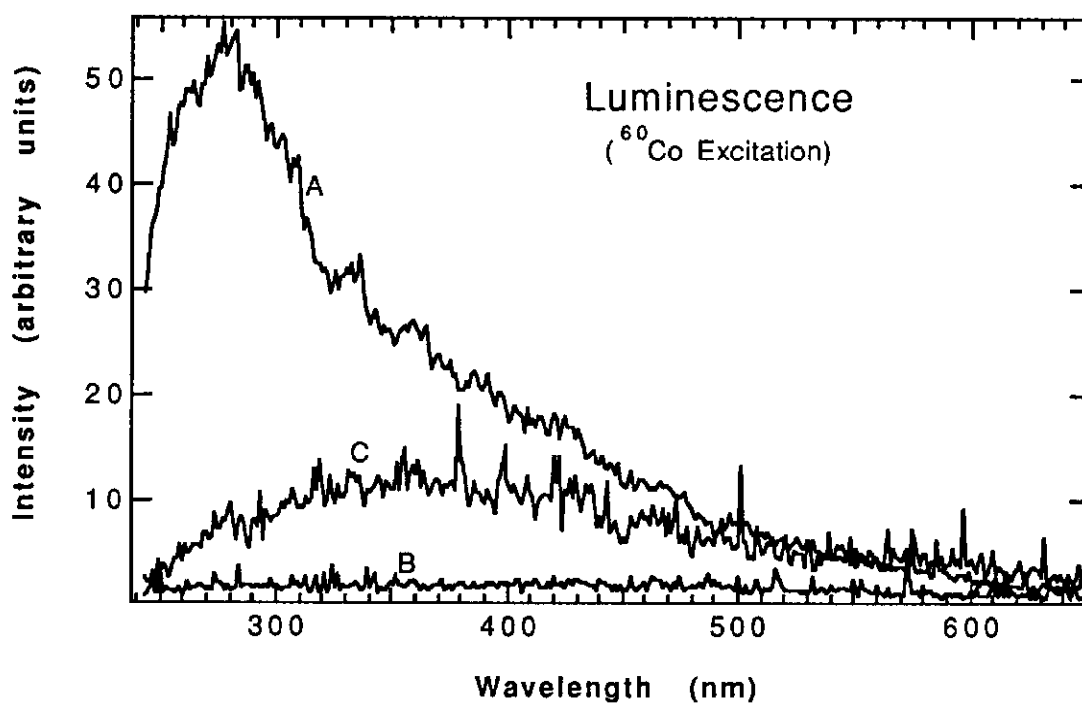


Figure 2 Luminescence spectra for three  $\text{PbF}_2$  samples: A, cubic; B, orthorhombic with micro fractures; and C, orthorhombic with clear domains.

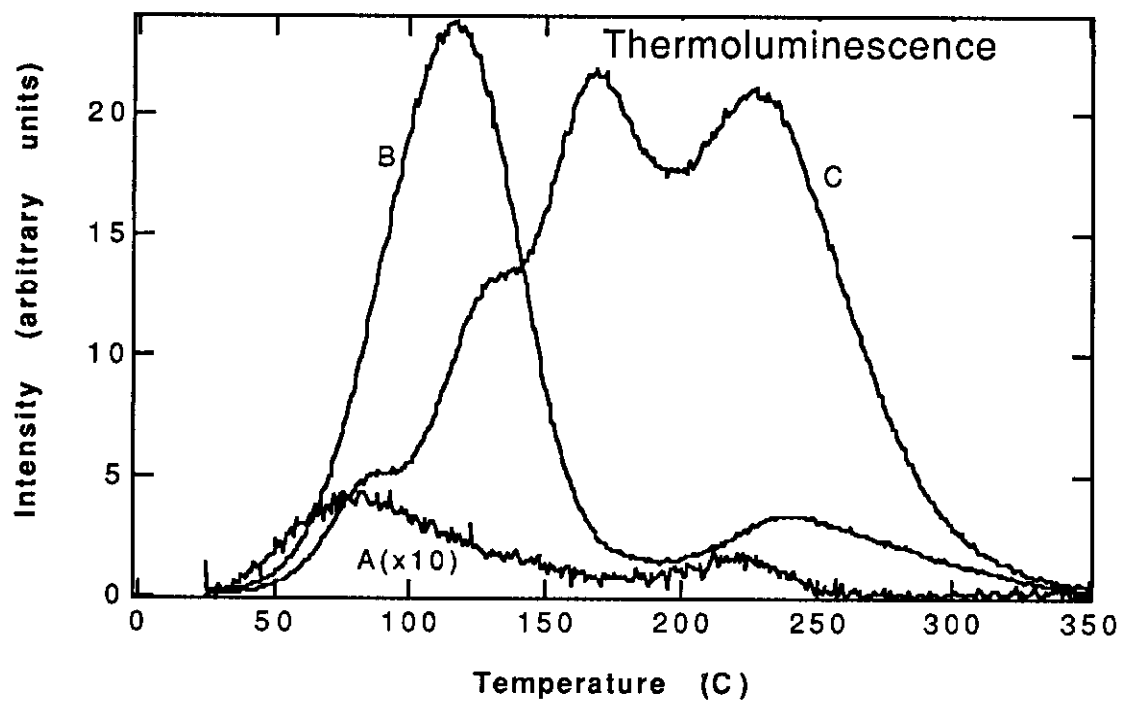


Figure 3 Thermoluminescence intensity as a function of temperature for three  $\text{PbF}_2$  samples: A, cubic; B, orthorhombic with micro fractures; and C, orthorhombic with clear domains.